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PRODUCTION OF HOLLOW GLASS MICROSPHERES FOR LASER FUSION TARGETS

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PRODUCTION OF HOLLOW GLASS MICROSPHERES FOR LASER FUSION TARGETS*

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ABSTRACT

Glass microspheres provide a convenient container for the deuterium-tritium fuel used in inertial fusion experiments. Stringent requirements as to size, uniformity and cleanliness necessitate initial production on a small scale. As part of the Laser Fusion Program, the Target Fabrication Group has developed processes to meet these demanding specifications.

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Lawrence Livermore National Laboratory is conducting the crucial laser fusion experiments to determine if burning of thermonuclear fuel can be initiated by focused laser beams. When a short pulse of light at extremely high power densities strikes a pellet containing the fuel, the resulting plasma is confined by its own inertia. Efficient thermonuclear burn requires confining the plasma for a sufficiently long time at extremely high temperatures and densities so that a large fraction of the nuclei fuse. One of the important elements in targets for these experiments is a thin hollow glass microsphere, produced to exacting specifications.

Early experiments with the DT (Deuterium-Tritium) fuel contained in thin, hollow glass microspheres (70 μm I.D. X 1 μm thick wall) achieved the necessary high temperatures. In these "exploding pusher" experiments, Figure 1, the laser beams rapidly heated the glass shell literally causing it to explode inward thus further heating and compressing the DT. Exploding pusher targets, however, compress the fuel to only a fraction of liquid DT density, much less than the 10^3 - 10^4 times liquid DT density needed for efficient burn. Higher densities are now being achieved by using longer laser pulses to drive thicker, coated glass microspheres, Figure 1. In this case the outer layers ablate more slowly, providing a rocket like drive which compresses the relatively cooler fuel to higher densities. To obtain both high temperature and density simultaneously will require the more powerful lasers being developed and even more advanced targets.

In the target designs pictured in Figure 1 the innermost layer next to the DT is a glass microsphere. Glass microspheres are used because they form

a convenient container for the fuel and the glass is acceptable from a design standpoint. The DT readily diffuses through the glass at 400°C but is trapped at room temperature. For high density targets, the glass spheres can be filled with DT prior to coating with the ablative layers that are not permeable to DT. This avoids using fill tubes or patching holes in the targets that would degrade the symmetry and thus the performance of the targets.

Spheres for the initial experiments were obtained by laboriously sorting batches of commercial spheres. Hollow glass microspheres serve a wide variety of needs, Table I. Commercially the emphasis is on producing spheres by the ton. Only one in about 10^5 of the spheres in preselected batches meets the relatively lax symmetry specifications for exploding pusher targets.

The glass-microsphere specifications for ablative laser fusion targets are very stringent. Acceptable shells must meet a diameter tolerance of $\pm$ 5 μm, a thickness tolerance of $\pm$ 0.5 μm, a wall thickness uniformity of 0.2 μm, and a surface smoothness of better than 0.05 μm. Because the glass microspheres undergo several additional processing steps which have low yields, we also need batches in which 80% of the spheres meet all of these requirements.

Since spheres for ablative targets are not available commercially, we have developed processes at LLNL for producing high quality microspheres in the needed sizes and quantities. Successful production of high quality glass

microspheres requires understanding and control of both the physics of sphere formation and the chemistry of glass. Table II indicates the improvement we have achieved in microsphere quality over the past three years.

MICROSPHERE PRODUCTION

During the past few years we have developed two primary methods of making hollow glass microspheres: the liquid-droplet method[1] and the dried-gel (frit) process. The liquid-droplet process is the more highly developed, reliably producing batches of microspheres 90% of which are within ± 10% of the same size and wall thickness. The dried-gel process allows more variation in the glass composition and makes it possible to produce much larger microspheres.

THE LIQUID-DROPLET PROCESS

This process starts with compounds which must be water soluble. Solutions begin with a sodium-silicate or Ludox[T.M.+] base to which various network formers or modifiers are added. This final mixture is formed into uniform droplets by acoustic disintegration of a liquid jet. Diameter control of these droplets is accomplished by variation of the orifice size, acoustic driving frequency, solution feed pressure and solution viscosity. These droplets pass through a long verticle furnace assembly, Fig. 2, where they inflate due to water encapsulation and fuse into hollow glass microspheres.

+ Dupont

The average transit time is highly variable and is a function of the microsphere size and furnace air flow. The system temperature profile and air flow, in conjunction with the drop size, determine the diameter, wall thickness, and uniformity of the spheres.

In the upper furnace section the droplets dehydrate and form a gel-like skin on their surface through which the rest of the water diffuses, depositing its solids. The drying temperature is critically important. If it is too low, the droplets dry to slowly, unnecessarily lengthening the required column. If it is too high, excessive vapor pressure ruptures the spheres. When vapor pressure and surface tension are balanced, the result is a hollow, relatively porous microsphere of dried glass-forming compounds.

In the lower, hotter zone of the furnace the gelled compounds melt, react, and fuse into hollow glass spheres. This step in the process depends critically on the choice of glass composition; the glass must have low viscosity to permit surface tension forces to distribute the material into uniform spherical walls. When properly tuned, the system produces batches in which more than 90% of the spheres have the same diameter and wall thickness within $\pm$ 10% (Fig. 3a). In addition, more than 90% of the spheres within a batch satisfy the exacting surface and symmetry specifications. Figure 3b is an interferogram of a batch of high quality spheres that illustrates both the high percentage with uniform walls and the narrow distribution of wall thicknesses.

The air flow through the liquid-droplet system is held to an absolute minimum to insure maximum transit time consistent with overcoming thermal convective updrafts. As a consequence of this, droplets entering the system slow to speeds much below that of terminal free fall velocity. Due to the use of driving frequencies in the audio range (2-10 kHz) it is necessary to selectively limit the number of droplets which actually enter the column. This is accomplished by charging individual droplets as they form and deflecting them away from the column opening. An electronic counter interfaced with the frequency generator and the charge ring permits a period (τ) adjustment. We therefore select $1/\tau$ droplets actually entering the system. Normal values of τ range from 20 to 50. For every 100 liquid droplets entering column top, usable glass microspheres amount to only 2-30%. The major loss is due to wall collisions during the forming process.

A standard size production microsphere at this facility is a 140 X 5. That is, 140 microns I.D. X 5 microns wall thickness. In order to emphasize the small quantities with which we consistently work, at an operating frequency of 5 kHz and τ = 25, a full days' production run ($\sim$4 hrs) produces 720,000 spheres or 0.58 grams of glass. In other words, to produce 1 lb. of these microspheres it would take approximately 780 days.

The liquid-droplet technique has two constraints: the glass-forming compounds must be in solution, and there is an upper limit on the droplet size. Some of the compositions we tried were unsuitable because they formed a gel in the reservoir of the droplet generator, clogging the nozzle. Others

became too viscous at normal concentrations or required too large a droplet size when diluted to a workable viscosity; hence, they failed to dry completely in our longest furnace. Thus, to expand the range of compositions and microsphere sizes available to us, we developed a dried-gel process to supplement the liquid-droplet method of microsphere production.[2]

THE DRIED-GEL PROCESS

In the dried-gel process,[3] we dry a bulk solution of glass-forming oxides and grind the hard residue into fine particles. Sieving selects a batch of roughly sized particles, which we then pass through a furnace. Trapped water of hydration inflates the particles as the surface starts to melt, forming hollow glass microspheres. The average transit time for this process is about the same as for the liquid-droplet process.

The furnace for the dried-gel process is similar to that for the liquid-droplet method without the upper drying section. This allows us to make the refining section much longer, which enables us to make relatively thick microspheres of high quality. In general, the longer and hotter the furnace, the better the sphericity and concentricity of the microspheres.

Not having to pass the solution through a small orifice gives us greater flexibility in composition, but the necessarily nonuniform particle size produces a wide variation in sphere size (Fig. 4). Furthermore, sieving the product to narrow the size distribution still leaves different wall

thicknesses (gel particles with different masses can result in spheres with the same diameter).

Production far surpasses that of the liquid droplet system, however. There is little inhibition of the feed rate for the dried-gel and consequently large batches approaching 2-3 grams can be produced easily. When necessary we density-cut sized microspheres by flotation in various liquids to narrow the wall-thickness distribution. We are also developing ways to produce spherical gel particles with uniform mass that could be sieved before entering the furnace for improved uniformity.

The dried-gel compositions are similar to those used in the liquid-droplet system. For our intial experiments with the composition we were able to make more massive spheres (140 μm I.D. with walls 20 μm thick). We can also produce oversize, thin-walled spheres (500 μm I.D. with walls 0.5 to 1 μm thick) by adding urea to the gel as an additional blowing agent.

Our two processes enable us to make a wide variety of hollow glass shells. Figure 5 illustrates the sizes and wall thicknesses obtainable.

GLASS COMPOSITION

Among the various glass forming compounds, only the alkali silicates are water soluble to any significant degree. Of the alkali silicates, the sodium oxide-silicon dioxide binary system (Na_2O-SiO_2) most easily forms a glass

at low temperatures. We chose a composition of about 22% Na_2O and 71% SiO_2 because it is close to the eutectic composition. This particular glass also has a lower viscosity below 1200°C than other alkali glasses, a vital consideration to ensure high sphericity and concentricity of the microspheres.

However, pure sodium silicate glass is highly susceptible to attack by atmospheric moisture. The primary mechanism appears to be the rapid formation of sodium hydroxide at the surface, which etches the underlying glass. The relatively rapid diffusion of sodium ions through the glass structure enhances this process.

Accordingly, we alter the Na_2O-SiO_2 system by adding small amounts of a network modifier (potassium oxide) and the network former boron oxide.

SURFACE TREATMENT

Even with a network modifier in the composition, however, the resulting glass still has reactive alkali on the surface, and the sodium ions retain some mobility. It is imperative, therefore, to wash and passivate the microspheres soon after they are formed. Conventional washing with hydrochloric or hydrofluoric acid removes the initial alkali, but the surfaces still deteriorate within a few days on exposure to humid air because of etching by sodium hydroxide that rises to the surface.

We have developed an acid wash procedure that significantly inhibits this etching. The procedure involves several washings with hot 0.5 N nitric acid combined with dilute ammonium fluoride, followed by rinses in hot distilled water, acetone, and ethanol. Microprobe analysis reveals that this wash procedure leaches out most of the sodium from the outer layers ($\sim$ 1 μm) of the microsphere wall.

Microspheres so treated show no deterioration even after several weeks of exposure to humid air. Figure 6 is a photograph made with the scanning electron microscope of the surface of one of our microspheres. Surface smoothness is much better than the required 500 nm, easily fulfilling the requirements for ICF targets.

It is not enough to produce a smooth glass surface that resists weathering. Storage of production batches of varying sized spheres is necessary to meet the variety of program needs.

Freshly washed microspheres are placed in glass vials filled with ethanol (200 proof). To insure a tight seal, teflon cap liners are added and parafilm$^{T.M.+}$ is stretched over the cap and vial. Glass microspheres stored with this technique have surfaces as good as those depicted in Figure 6 after 9 months in the vials.

+ American Can Company

SPECIAL GAS FILLS

After making glass microspheres of the required perfection, we must fill them with fuel gas, a mixture of deuterium and tritium (DT). As mentioned earlier, the glass is permeable to such hydrogen isotopes when hot. Filling is a matter of exposing the microspheres to a high pressure of DT mixture in an oven at 400°C for a day or so.

For diagnostic purposes, however, we would sometimes like to include a partial fill of some other gas. Argon, for example, emits a distinctive x-ray line whose width depends on the fuel density; it can thereby serve as a direct measure of the implosive compression in targets whose glass walls are thin enough to pass the x rays. Bromine, on the other hand, would absorb neutrons from the fusion reaction and become radioactive. If we independently measure the total energy released, we can determine from the amount of bromine radioactivity how dense the fuel had become at the time of nuclear burn.

Unfortunately, the permeation rate for such gases is a million times less than that for hydrogen isotopes under similar conditions. To introduce them into the microspheres by permeation, we would have to alter the glass composition and then subject the microspheres to high temperatures and pressures for a very long time. Such a procedure would probably be self-defeating, however, devitrifying the glass, roughening the surface by alkali precipitation, and distorting the symmetry because of the prolonged stress.

With our techniques of producing microspheres, however, we can add the nonhydrogen gas during sphere formation.[4] We simply replace the air in the furnace with the gas in question, which diffuses through the walls and remains trapped after the spheres form. On the average, we obtain partial pressures of 20 kPa at room temperature inside our microspheres. We have already used argon gas fills in exploding-pusher experiments and recently developed a way to add bromine to ablative targets.

ABLATIVE TARGETS

The flexibility inherent in these microsphere fabrication techniques has enabled us to develop ablative targets capable of achieving much higher fuel densities. These consist of thicker glass microspheres coated with a layer of fluorocarbon plastic. The laser pulse, which is much longer and may be specially shaped to regulate the appearance of shock waves, burns off the plastic layer at a rapid but controlled rate. The rapid expansion of gases from the ablative layer provides an extended rocketlike inward thrust that compresses both the glass shell and the enclosed, relatively cooler fuel to higher densities.

Because the entended thrust of the ablation produces much higher implosion velocities, it also magnifies the effects of imperfections in the glass microsphere. Hence microspheres for ablative targets must have far more uniform walls and smoother outer surfaces than exploding pushers do. Furthermore, microspheres for ablative targets need much thicker walls than

are found in the commercial microspheres. We were able to produce such targets only because we had developed our own microsphere production equipment.

SUMMARY

We have developed our own production facility to provide hollow glass microspheres meeting the requirements of the ICF program. Control of the production parameters enables us to improve greatly the reproducibility of the process, to vary the composition of the glass and of the fill gas, and to expand the choice of dimensions available. We have also brought under control many of the mechanisms that form surface defects, greatly reducing reject rates. The availability of large batches of target-quality microspheres has made it possible to progress to ablative coated targets, the next phase in our development of ICF targets.

ACKNOWLEDGEMENT

This production facility would not have been possible without the competent assistance of a wide range of professional and technical staff both within the Target Fabrication Group of the Laser Fusion Program and the Laboratory as a whole.

TABLE CAPTIONS

Table I. Commercial Applications of Glass Microspheres.

Table II. Target-fabrication yields, illustrating the improvement we have been able to achieve by choice of glass composition and control of process parameters.

FIGURES

Figure 1 Representative ICF target designs. (a) Exploding-pusher target. (b) Intermediate-density ablative target, coated with a layer of fluorocarbon plastic. (c) Multishell design.

Figure 2 The liquid-droplet process for forming hollow glass microspheres. A jet of glass-forming metallic oxides in aqueous solution entering the oven from the top is broken into a stream of droplets of uniform size by acoustic vibration. As the droplets fall through the oven they are first dehydrated, forming porous shells of gelled solids, and then fired to fuse the solids into glass. Control of the process parameters, particularly the temperature profile and air flow in the oven and the composition and size of the droplets, enables us to keep the diameter, wall thickness, and surface finish within acceptable limits.

Figure 3a Uniformity of microspheres produced at the rate of 100 spheres a second by the liquid-droplet process. Histogram showing the distribution of outside diameters. About 90% of the microspheres have the same diameter within $\pm$ 10%.

Figure 3b Interferogram showing wall-thickness uniformity (80% have the same thickness within $\pm$ 13%). More than 90% of the spheres satisfy the stringent symmetry requirements for ablative targets.

Figure 4 Particles of dried gel (a) and glass microspheres blown from them (b). Although this process produces a wider size distribution than the liquid-droplet method, it permits use of a wider variety of glass formulations.

Figure 5 Combinations of glass microsphere diameter and wall thickness available from commercial suppliers and from our two alternative processes. For most of our current target designs, the microsphere specifications fall outside the commercial supply area on this graph.

Figure 6 Scanning electron microscope photograph of the surface of a glass microsphere after being washed with dilute nitric acid to neutralize alkali contamination and to passivate the surface against attack by atmospheric moisture. Wall-uniformity defects are less than 4%; the surface finish is smooth to within 10 to 20 nm.

REFERENCES

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COMMERCIAL APPLICATIONS OF GLASS MICROSPHERES

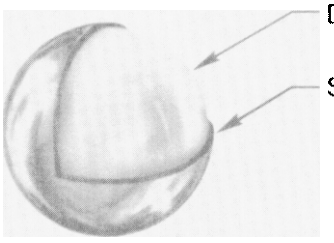
Boat construction	**putties, sealing compounds; filler for hull and deck structures; plastic components (rudders, hatch covers, etc.)**
Building materials	**synthetic brick, cultured marble; filler for gypsum board**
Explosives (construction/mining)	**filler for slurried explosive compositions**
Furniture	**extender for plastic decorative and structural components**
Plastics, rubber products	**extender for cast plastic components; extender for spray up fiberglass reinforced fabrication**
Sporting goods	**extender for bowling ball cores**
Paints/coatings	**textured coatings**
Pulp and paper manufacturing	**filler**

Target-fabrication yields, illustrating the improvement we have been able to achieve by choice of glass composition and control of process parameters.

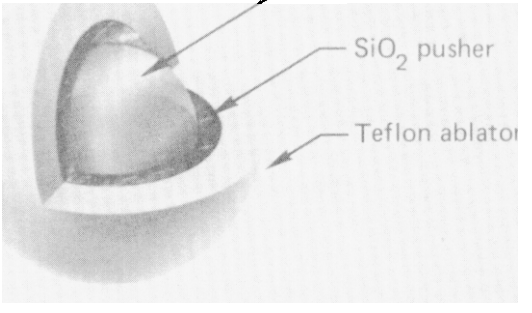
	Uncoated			Coated	
	Commercial	**LLL**		**Commercial**	**LLL**
Initial batch[a]	100 000	100 000	**Initial batch**	Suitable	100 000
After sieving for size	10 000	90 000	**After sieving for size**	spheres	90 000
After crush test and D-T load	1 000	60 000	**After crush test and D-T load**	not available	60 000
After optical selection	1	50 000	**After coating with ablative layer**		20 000
			After optical selection		10
Yield	1/100 000	1/2	**Yield**	None	1/10 000

[a] After a 10:1 preselection screening of commercial lots.

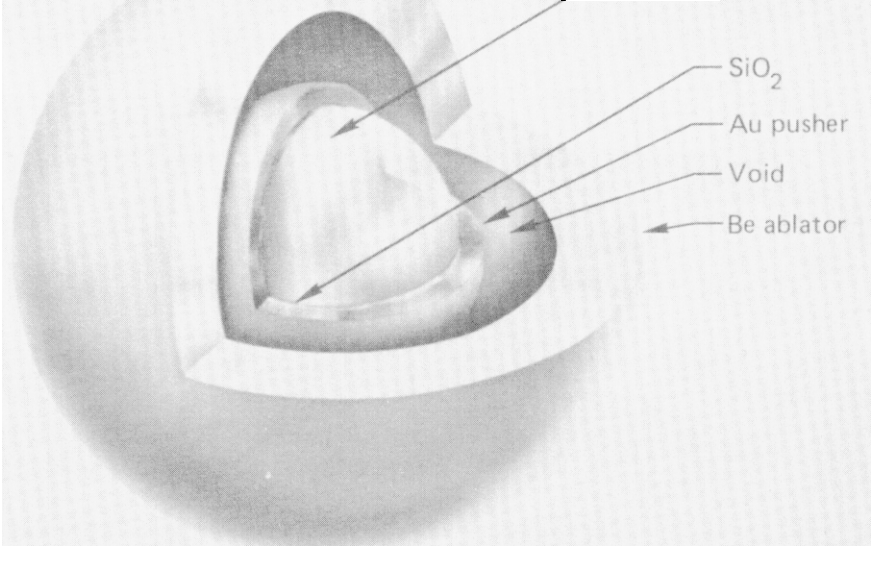
a)

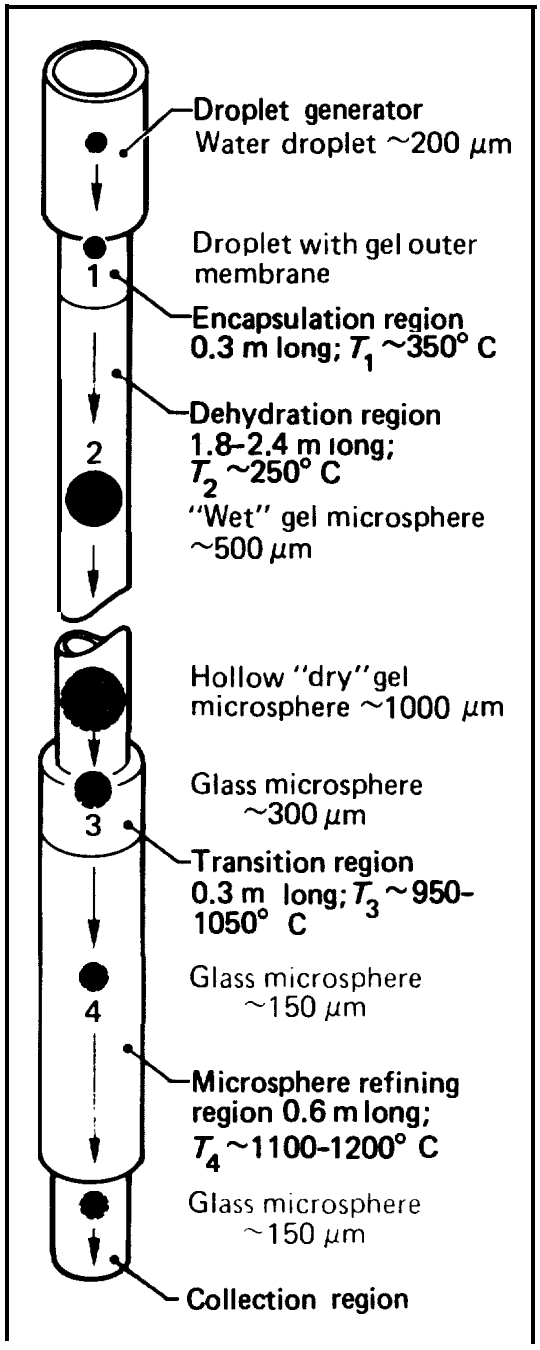

D-T gas fuel
SiO_2 pusher

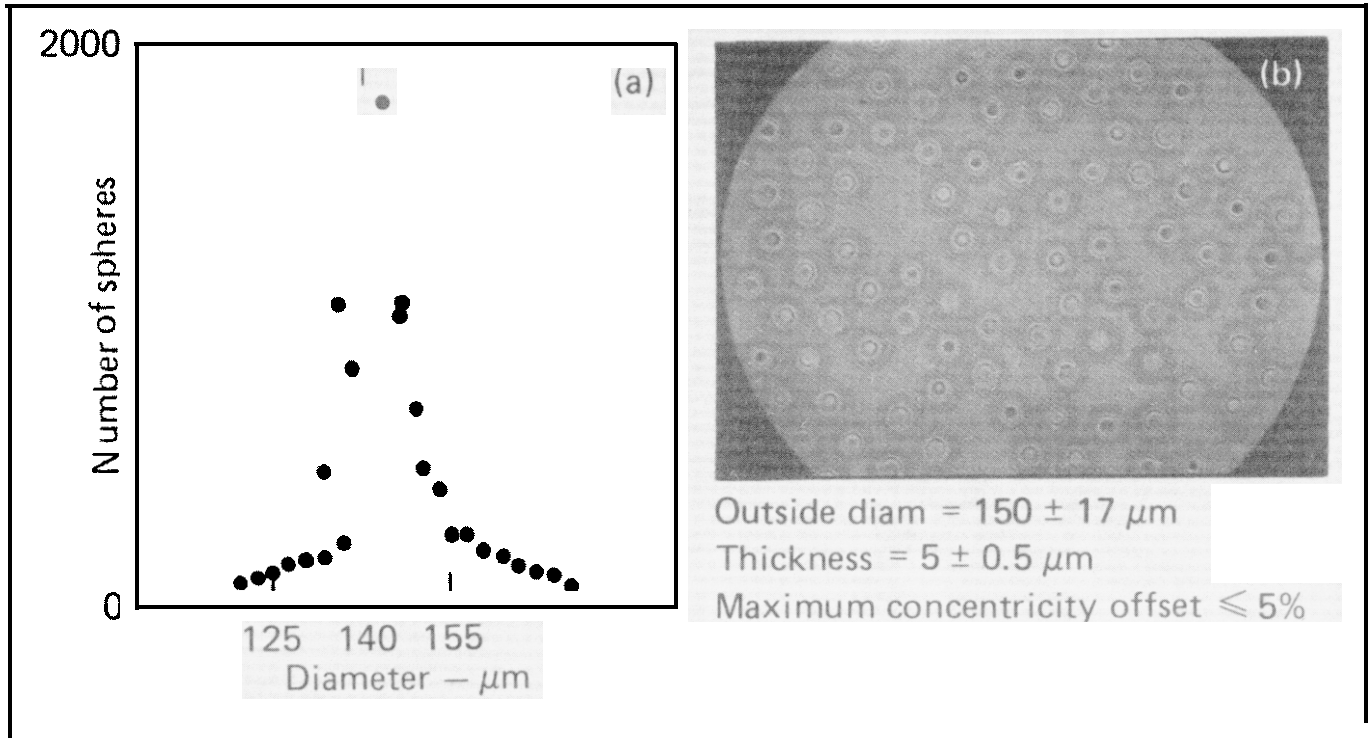
(b)

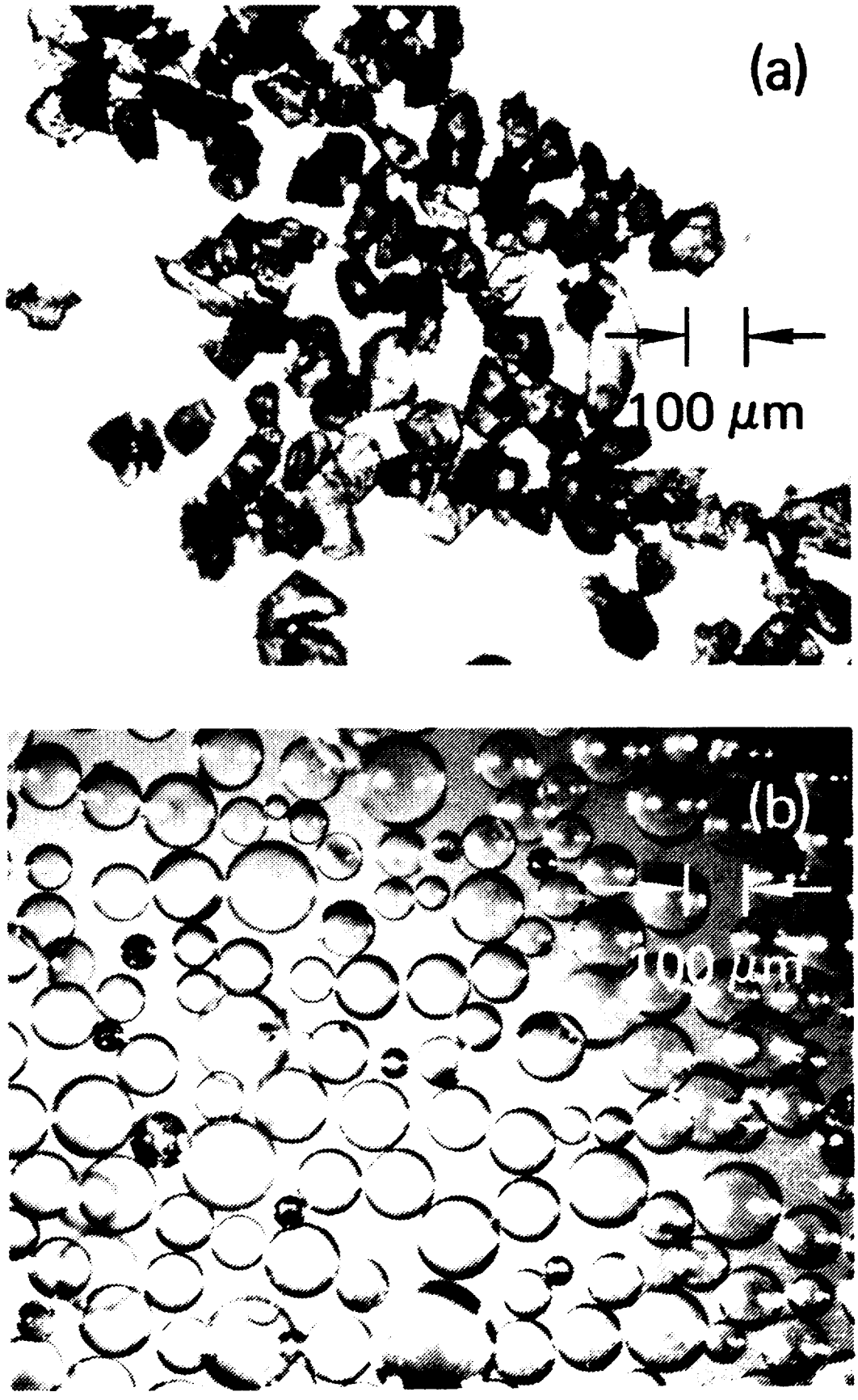

D-T gas fuel
SiO_2 pusher
Teflon ablator

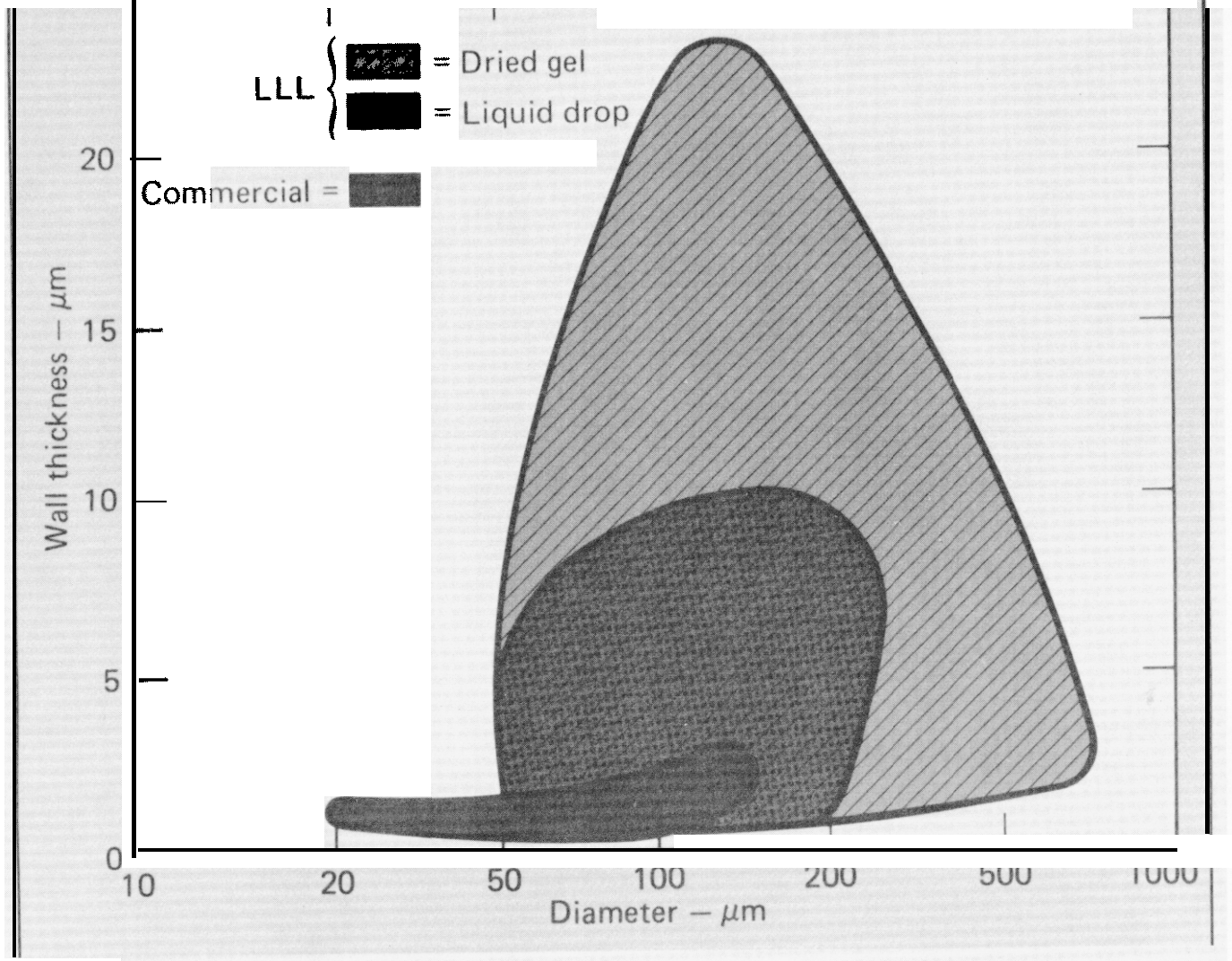
(c)

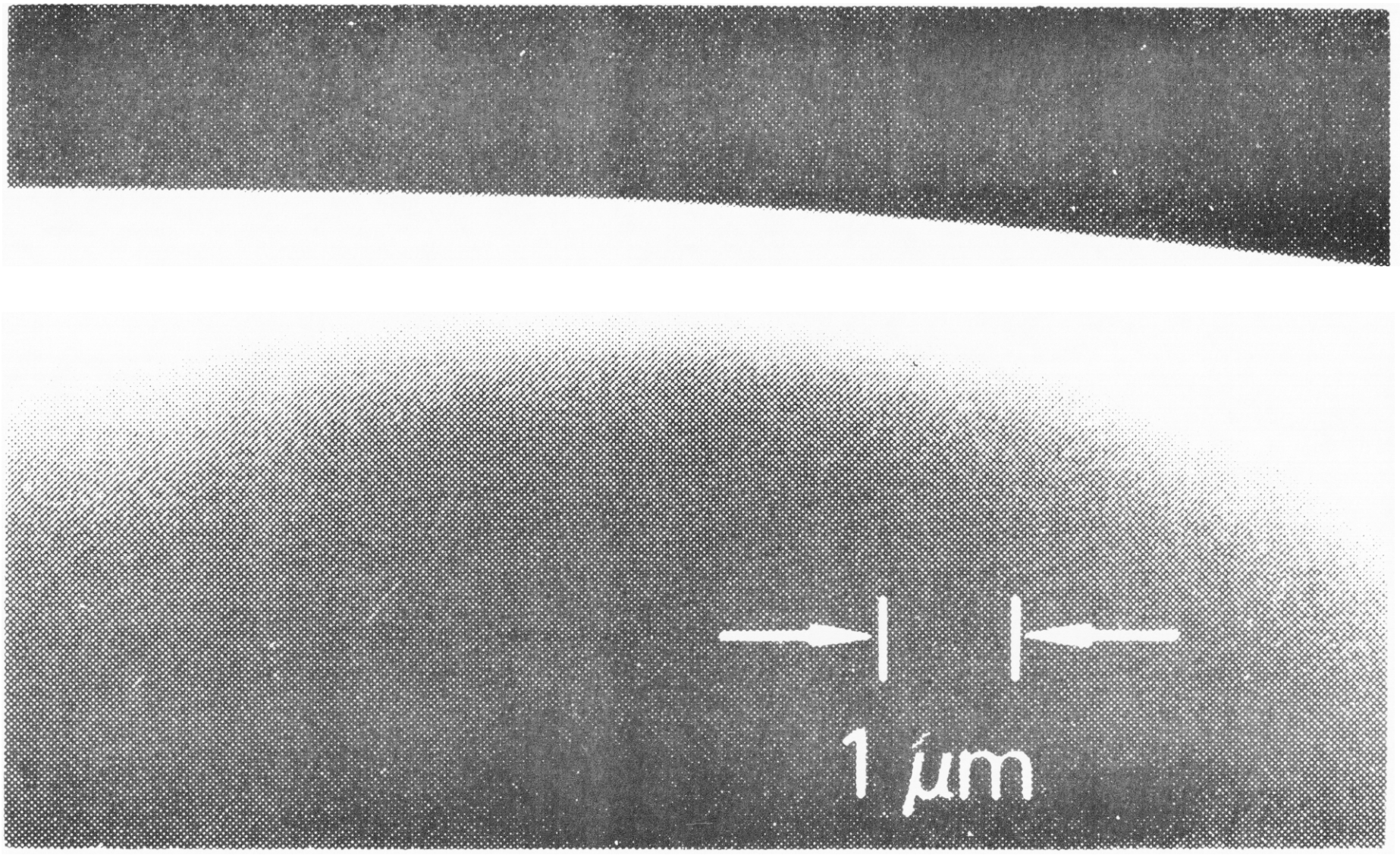

D-T gas fuel
SiO_2
Au pusher
Void
Be ablator


Droplet generator
Water droplet ~200 μm
Droplet with gel outer membrane
1
Encapsulation region
0.3 m long; T_1 ~350° C
Dehydration region
1.8–2.4 m long;
T_2 ~250° C
2
"Wet" gel microsphere
~500 μm
Hollow "dry" gel microsphere ~1000 μm
Glass microsphere
~300 μm
3
Transition region
0.3 m long; T_3 ~950–1050° C
Glass microsphere
~150 μm
4
Microsphere refining region 0.6 m long;
T_4 ~1100–1200° C
Glass microsphere
~150 μm
Collection region


2000
0
Number of spheres
(a)
125 140 155
Diameter — μm
(b)
Outside diam = 150 ± 17 μm
Thickness = 5 ± 0.5 μm
Maximum concentricity offset ⩽ 5%


(a)
100 μm
(b)
100 μm


LLL
= Dried gel
= Liquid drop
Commercial =
20
15
10
5
0
Wall thickness — μm
10
20
50
100
200
500
1000
Diameter — μm


1 μm